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## Optimization of *Jatropha curcas* pure plant oil production

Subroto, Erna

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# Chapter 5

## **Solvent-assisted mechanical extraction of oil from *Jatropha curcas* L. kernel**

Erna Subroto, Robert Manurung, Hero Jan Heeres, Antonius Augustinus Broekhuis

Submitted to Industrial Crops and Products

## Abstract

For rural areas mechanical extraction is considered to be the most versatile option for oil expression from *Jatropha curcas* L. seeds. In previous research, 87% d.b. of oil recovery was obtained by conventional pressing, leaving 13% d.b. of residual oil in the cake. In order to improve the extraction efficiency, solvent addition was evaluated in this study. The ranges of parameters investigated were: applied pressure (5-25 MPa), pressing temperature (25-105 °C), type of alcohol (ethanol and butanol), solvent to kernel ratio (0.14-0.56 v/w) and moisture content (0-10% v/v) variation for ethanol.

Screening experiments showed that the addition of solvents gave a more efficient oil recovery. Ethanol addition gave higher oil recovery than butanol, despite the drawback that the pressing temperature is limited by its low boiling point of 78 °C. Butanol as solvent allowed for a higher pressing temperature, i.e. up to 117 °C. However, ethanol is preferred due to its easy separation from the obtained oil. It is found that the moisture content of ethanol has a strong influence on oil recovery, with anhydrous ethanol giving better recovery than aqueous ethanol. An oil recovery of 93.3% d.b. is achieved when jatropha kernel with moisture content of 3.8% w.b. is pressed at 78 °C, a pressure of 15 MPa at an ethanol to kernel ratio of 0.14 v/w using ethanol 99.9% v/v as extracting solvent.

**Keywords:** renewable solvents, ethanol, butanol, hydraulic press, *Jatropha curcas* L., oil extraction

## 5.1 Introduction

The extraction of oil from jatropha seeds can be performed by mechanical rupturing of cells in a conventional pressing operation. However, the extraction efficiency is limited and depends on processing parameters such as: applied pressure, temperature, time, shell content and the presence of moisture in the raw material. Optimization studies so far resulted in an oil recovery of 87% d.b. [1,2], while the resulting press-cake still contains 13% d.b. of residual oil.

Some two decades ago, gas-assisted mechanical extraction using Sc-CO<sub>2</sub> (supercritical carbon dioxide) has been proposed by Rice (1992) [3]. This method is a combination of mechanical expression and the use of supercritical carbon dioxide. The advantages of this method are that more oil is recovered without compromising quality and the process operates at lower temperatures than the ones used in the conventional pressing [4,5]. However the complexity and costs of the process are major disadvantages.

Regular solvent addition can be used to increase extraction efficiency as it can facilitate the diffusion of the soluble compounds and the release of oil. Solvent-assisted extraction of sunflower oil in a twin screw extruder has been explored by Dufaure et al., (1999) [6]. The authors used acidified alcohol (2-Ethylhexanol mixed with phosphoric acid) as the extracting solvent and achieved a 15% increase in oil recovery compared to non-solvent extraction. It is assumed that solvent addition promotes the oil recovery by solubilizing triglycerides. The high oil miscibility at room temperature requires solvent recovery by distillation rather than by phase separation. The former is more energy intensive due to high boiling point of the solvent (184.6 °C). Evon et al., (2007) [7] tested water as the solvent for sunflower oil extraction in a twin screw extruder, but achieved only a low recovery level of 55% d.b.

The use of ethanol as an extracting solvent has been studied since the beginning of the 1900's. Several studies have shown that these extractions yield good quality oil and cake, and enable better extraction of sugars, free fatty acids, phospholipids, pigments and waxes compared to hexane extraction [8]. Ethanol has been studied for oil extraction from soybeans [8], corn [9], sunflower seed [10], and cottonseed [11]. Ethanol is the preferred solvent to evaluate as it may be produced from renewable resources and is one of the four vegetable oil solvents (water, ethanol, butane and propane) that are considered as safe by the US Food and Drug Administration. In addition, although it is flammable (flash point= 8.9 °C; ignition temperature = 425 °C), ethanol has less handling risks than hexane (flash point = -23 °C; ignition temperature= 225 °C) [12].

Ethanol offers high oil solubility at elevated and limited solubility at ambient temperatures. This temperature dependence of oil solubility provides the basis for the extraction process, permitting oil recovery by cooling and phase separation rather than by distillation. This is

considered desirable since cooling requires less energy than distillation [13]. Subsequent solvent stripping from the oil-rich phase and solvent recovery from the solvent-rich phase can easily be carried out because of the high difference between the boiling point of ethanol and oil. These operations can be accomplished by distillation at temperatures below 80 °C. In addition, all compounds soluble in ethanol will be recovered. This is expected to be an advantage of the ethanol extraction process since the soluble compounds such as phospholipids (mainly phosphatidylcholine or lecithin) have important value as emulsifiers.

The aim of this study is to evaluate the effect of ethanol addition on oil recovery and to maximize the recovery of good quality oil and usable protein-rich press-cake.

## **5.2 Material and methods**

### **5.2.1 Materials**

Dried *jatropha* seeds were obtained from a *jatropha* plantation in Ciamis, West Java, Indonesia. The seeds were harvested manually during July 2010, sun-dried and stored in jute bags in a warehouse facility at temperatures between 20-30 °C and at a relative humidity of 60-70% for one month. The material was transported to The Netherlands, in August 2010. After transport, the seeds were stored at room temperature at (15-25 °C) and a relative humidity of 40-50%. The seeds were deshelled manually and the kernels were conditioned to moisture contents of  $\pm 3.8\%$  w.b. The kernels were used directly in the pressing experiments to reduce the influence of storage time and conditions on oil quality. The oil content of *jatropha* kernel was 61.4% d.b. with the original moisture content of kernel in the range of 7 - 7.2% w.b. The oil analyses were conducted directly after pressing in September 2010.

Solvents used in this work were anhydrous butanol (99.5%; Merck, Germany) and anhydrous ethanol (99.9%; Merck, Germany). Aqueous ethanol with water content of 5 and 10% by volume were prepared by addition of deionized water to anhydrous ethanol. Potassium hydroxide (pellets, 85%, Vetec), oxalic acid anhydrous ( $\geq 99\%$ , Sigma-Aldrich), diethyl ether ( $\geq 99\%$ , Sigma-Aldrich), hexane ( $\geq 99\%$ , Sigma Aldrich), Hydranal solvent (Fluka) and Hydranal titrant 5 (Fluka) were bought from Sigma-Aldrich (Amsterdam, The Netherlands).

### **5.2.2 Moisture conditioning**

Based on the result from a previous study [2], the optimum moisture content was taken as 3.8% w.b. For oil recovery measurement, the kernels were conditioned by heating at 40 °C for a period of time until the moisture content of 3.8% w.b. was achieved. The kernels were

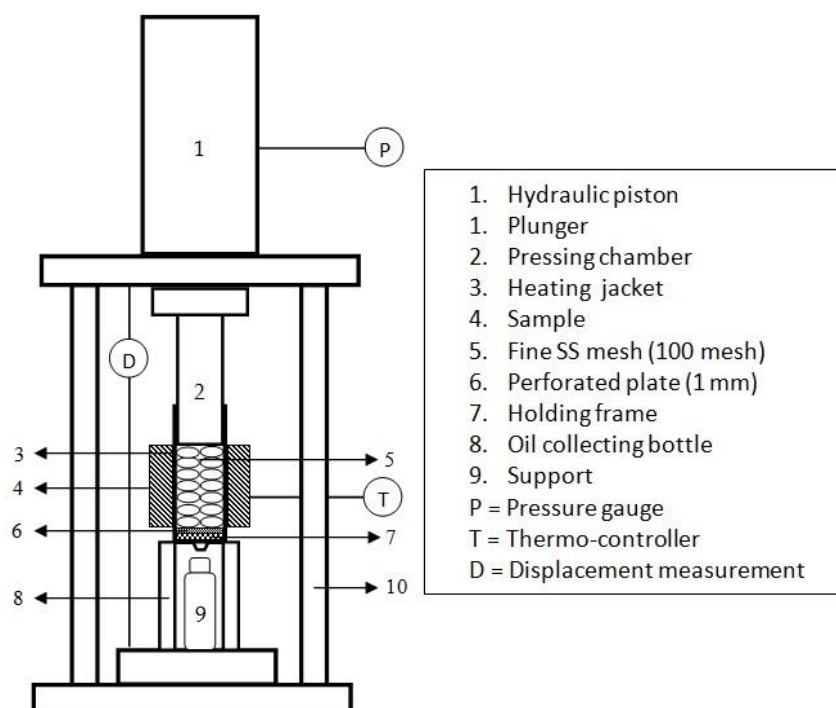
tightly wrapped in a low-density polyethylene bag of 25  $\mu\text{m}$  thickness and then put inside a desiccator containing silica gel for at least 1 day before being pressed. For oil quality analysis, the kernels were stored in the desiccator containing silica gel for equilibration until they reached the desired moisture content and then wrapped in the polyethylene bag. Moisture content after conditioning was determined by calculating the weight difference of the sample before and after conditioning. The total moisture content of the sample before the pressing experiment was verified by oven drying at 105  $^{\circ}\text{C}$  until constant weight.

### 5.2.3 Hydraulic pressing

A specially designed laboratory hydraulic press was used to study the effect of solvent on the recovery of oil from the jatropha kernels. A schematic representation of the press is shown in Figure 1. The pressing chamber is made of stainless steel with a diameter of 20 mm and a height of 70 mm. Sample is placed inside the chamber above a perforated plate (diameter of 1 mm) covered with a fine stainless steel mesh (100 mesh) placed at the bottom of the pressing chamber acting as filter during extraction. An electrical-resistance heating ring being attached around the pressing chamber is used to preheat the pressing chamber during operation within a temperature range of 30–105  $^{\circ}\text{C}$ . For expression at 25  $^{\circ}\text{C}$ , the heating ring was removed. Pressures up to 25 MPa were applied by a hydraulic plunger. The press is equipped with a thermocouple ( $\pm 1$   $^{\circ}\text{C}$ ), pressure measurement ( $\pm 1$  MPa), and a level indicator ( $\pm 0.01$  mm), which measures the distance the plunger traveled.

Approximately 7 g of sample is placed in the pressing chamber. Afterwards, the plunger is put on top of the sample. The sample is equilibrated at the pressing temperature for 5 min. After this, the mechanical pressure is increased linearly at a pressing rate of 0.125 MPa/s until the desired pressure is reached. After 5 min of pressing, the plunger is loosened, up to 4 ml of solvent is added and the cake is again pressed for the next five min. Total pressing time is 10 min. At least three replicate measurements were performed for each sample and average values were taken.

For the pressure step experiments, the pressure was increased stepwise from 5 to 25 MPa every 2 min thus adding up to a total pressing time of 10 min. For the solvent-assisted experiment: after 2 min of pressing at 5 MPa the pressure is relieved, ethanol is added and the pressure is re-applied for the next 2 min at 10 MPa. This procedure is repeated 3 times with an increase in pressure of 5 MPa per step. For the 25 min pressing experiment the same procedure was used except that the pressure time interval was increased from 2 to 5 min. At every pressure improvement, the solvent was added at a solvent to kernel ratio of 0.14 v/w. Thus for a total of 4 solvent additions, the total solvent to kernel ratio would be 0.56. The solvent used was ethanol 95% v/v.



**Figure 1** Schematic representation of the hydraulic press

#### 5.2.4 Total oil content and oil recovery

The oil content of the sample was determined using standard Soxhlet extraction methods. The kernels were dried overnight in an oven at 105 °C before analysis. The dried kernels were grinded using a coffee grinder (Princess 242195, Netherland) and approximately 10 g samples were transferred into a cellulose extraction thimble. This was extracted with 100 ml n-hexane at its boiling point for 24 hours. The solvent was removed using a rotary vacuum evaporator (100 mbar 40 °C). The total oil content is calculated on a dry basis of the sample.

For pressing experiments, the oil weight is the oil collected in the bottle after each experiment and after solvent evaporation. Residual ethanol and butanol were removed by drying in the oven at 80 °C and 120 °C until constant weight, respectively. The oil recovery is defined as the ratio of the amount of oil expressed (after solvent removal) to the total oil content of the sample at dry weight basis.

#### 5.2.5 Oil quality analysis

For oil quality analysis, two methods of ethanol removal were performed: first by phase separation using a centrifuge (2,000 x g for 10 min, 25 °C) and second, by ethanol

evaporation under vacuum at 30 °C and 100 mbar. The oils were recovered and further used for oil analysis. Chemical analyses of the samples were carried out according to the standard test methods: DIN EN 14104, DIN EN ISO 12937, DIN EN 14112 and DIN EN 14107 for acid value, water content, oxidative stability and phosphorus content, respectively. According to the German fuel standard DIN 51605:2010-10 for pure plant oil, the acid value, phosphorus content, and water content should not exceed 2 mg KOH/g oil, 3 ppm, and 750 ppm, respectively, and the oxidative stability should be at least 6 h. The latter is evaluated as the Oxidative Stability Index (OSI) expressed in hours Induction Period (IP) and is measured using a Rancimat Model 873 Apparatus (Metrohm AG, Herisau, Switzerland) in accordance with the Rancimat method EN 14112. Most of the chemical property analyses of plant oil samples were conducted in our laboratory with the exception of phosphorus content analysis which was conducted by ASG Analytik-Service GmbH, Germany. Duplicate measurements were performed on each sample and average values are reported.

#### *Determination of non-lipid contaminants from the oil*

After ethanol removal, the oil was determined for the non-lipid content. The tests were carried out by blending the oil with 25 ml of methanol: water (1:1) (v/v) for 5 min with magnetic stirrer, this being followed by a 5-min quiescent period. After addition of 25 ml hexane to the mixture and subsequently shaking for 5 min, the mixture was left for a 4 hours quiescent period. The upper phase which is oil dissolved in hexane was skimmed off. The aqueous phase was re-extracted three times with hexane at an (methanol: water)-to-hexane ratio of 2:1 (v/v) to recover any residual oil. Both phases were evaporated under vacuum to recover oil and dissolved solids (non-lipid contaminants), respectively.

### **5.3 Results and discussions**

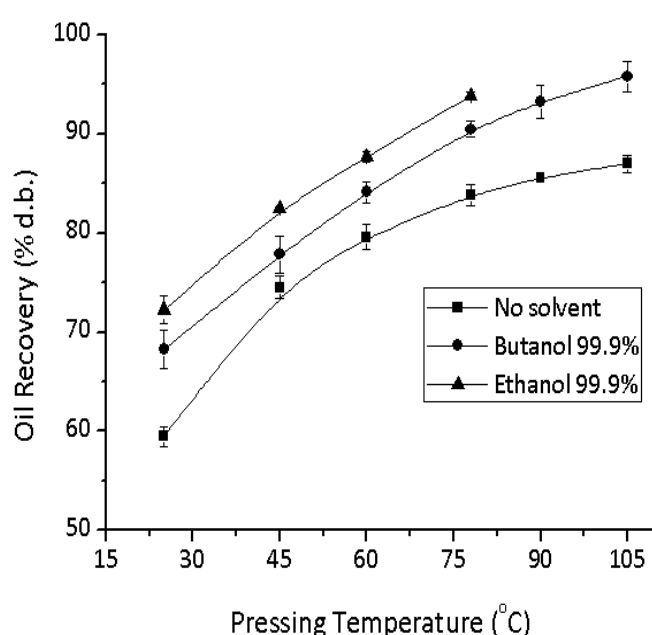
#### **5.3.1 Comparison of solvents**

Ethanol and butanol were used as the solvents in this experiment as these can be produced from renewable resources via fermentation [14]. Addition of ethanol resulted in a higher oil recovery than found for butanol (see Figure 2). The lower oil recovery for butanol is in contrast with the higher oil solubility in butanol compared to ethanol. The solubility of oil in alcohols increases with the chain-length of the hydrocarbon moiety of the alcohol, thus vegetable oils are to some extent soluble in ethanol and completely soluble in butanol.

Solvent extraction of vegetable oil from oilseed involves capillary flow of free oil from ruptured cells and diffusion of the oil from un-ruptured cells. The larger portion of oil is readily available from ruptured cells and is directed into inter-kernel voids. The oil is transferred through the compressed cake by capillary flow. According to Johnson (2008) [15], the rate of oil transfer is partly dependent on viscosities of solvent and miscella



(solvent–oil emulsion). At higher temperatures the solvent viscosity becomes lower and fluidity of oil and solvent become larger thus leading to an increase in extraction rate. The higher viscosity of butanol negatively affects the capability to increase the fluidity of the oil compared to ethanol. Butanol has a viscosity approximately twice the viscosity of ethanol in the temperature range studied. Viscosity of butanol and ethanol at 25 °C were 2.545 and 1.081 mPas, respectively; the viscosity of butanol and ethanol at 78 °C are 0.788 and 0.456 mPas, respectively [16]. Johnson (2008) [15] mentioned that the smaller portion of oil contained in un-ruptured cells is diffused out of the cell by osmosis. This transfer rate has been shown to be very slow in oilseed extraction, and the rate depends on the molecular sizes of the oil and the solvent.



**Figure 2** Effect of solvent and pressing temperature on oil recovery from jatropha kernel pressed (solvent to kernel ratio was 0.14 v/w, absolute alcohol, moisture content of kernel 3.8% w.b., applied pressure 15 MPa)

From the range of temperatures studied, solvent-assisted pressing at 25 °C gave the highest oil recovery increment of 12.73% and 8.76% for ethanol and butanol, respectively. In general, the oil cells are primarily ruptured due to the application of pressure, although heating is expected to weaken the cell walls and to denaturize the protein. At this low pressing temperature, the flow of the oil through the compressed cake is hampered. Addition of solvent helps to increase the fluidity of the oil and promotes extraction due to the lowered viscosity and, as a result, oil recovery increases.

### *Effect of Butanol addition at higher temperature*

Addition of ethanol is limited by its boiling point of 78.5 °C, which resulted in a maximum oil recovery of approximately 93.3% d.b. A further increase in temperature is expected to have a positive effect on oil recovery thus butanol was studied further at higher temperatures. Butanol has a boiling point, 117.2 °C.

Addition of butanol as the extracting solvent gave an oil recovery exceeding 95% d.b., in particular at 105 °C. However there is a drawback for using butanol as its high oil solubility at low temperatures cause difficulties in the oil-butanol separation. Distillation is considered as the only method for separating butanol from the oil. This method requires a high energy input compared to separating ethanol and oil by cooling and phase separation. Despite a slightly higher oil recovery with butanol (95.8% d.b. oil recovery when pressing at 15 MPa, 105 °C) compared to ethanol (93.3% d.b. oil recovery when pressing at 15 MPa, 78 °C), the latter is preferred for its easy separation from the oil. In addition, extraction at lower temperature gave a better oil quality and lower energy demand.

### **5.3.2 Effect of ethanol purity**

Experiments were performed with three different ethanol purities, namely 99.9, 95, and 90% v/v at a ratio of ethanol/kernels of 0.56 v/w (See Table 1). Ethanol purity of 99.9, 95 and 90% v/v gave oil recoveries of 93.7, 90.9, 81.7% d.b., respectively, against 83.9 for the solvent-free pressing. Water content in the solvent clearly affected the oil recovery of jatropha pressing. As the water content increases, ethanol becomes more polar and oil solubility dramatically decreases [17-18]. According to da Silva et al. (2010) [19] jatropha oil solubility at 60 °C in 99.9% and 94% v/v ethanol are 14.1 and 4.5%, respectively. The oil recovery of jatropha pressed with 90% v/v ethanol dropped even below the level reached for solvent-free pressing (81.7 for ethanol 90% v/v versus 83.7% for the latter). This is explained by the absorption of water from aqueous ethanol into the cake, thus increasing the moisture content of cake beyond the 4% w.b., which reduces the oil recovery [1]. When using ethanol 90%, it is observed that the water content in the recovered ethanol is decreased from 12.3% to 9.8%. This explains the absorption of water from ethanol into the cake (see Table 2).

Parameters that affect the quality of the oil include non-lipid content, acid value, phosphorus content, oxidative stability and water content. The data for the extracted oil by ethanol-assisted pressing are shown in Table 1. These samples contain more phospholipids, FFAs and non-lipid compounds. Non-lipid compounds usually include oil-soluble flavors, peptides, sugars and pigments [20]. Acid value is a measurement of the hydrolytic degradation of oil during storage or processing, i.e. the hydrolysis of ester bonds in lipids by

enzyme action or by heat and moisture results in the formation of FFAs. FFAs can accelerate autoxidation of vegetable oils [21]. Oxidative stability is associated with the oxidative degradation of oil which results in development of rancidity. A higher Oxidative Stability Index (OSI) expressed in hours Induction Period (IP) means more resistance to oxidation. Phosphorus content indicates the presence of phosphor-derived components in oil such as phospholipids and phytates.

**Table 1** Oil recovery and properties of solvent-assisted jatropha oil: effect of ethanol composition and work-up procedure.

Oil properties	No-Solvent	Ethanol 99.9%	Ethanol 95%	Ethanol 90%
Oil Recovery (% d.b.)	83.7±0.8	93.7±0.6	90.9±0.8	81.7±0.4
Non-lipid content (% d.b)	0.05	0.32	0.61	1.33
Ethanol removed by vacuum evaporation				
P (ppm)	0.5	95	140	100
AV (mg KOH/g oil)	0.3	0.47	0.58	0.72
Ethanol removed by centrifugation				
P (ppm)	0.5	92	84	76
AV (mg KOH/g oil)	0.30	0.29	0.32	0.38
IP (hours)	9.44	16.08	17.27	17.37
Water (%w/w)	0.087	0.15	0.23	0.30

Notes: a. Pressed at 15 MPa, 78°C for 10 min with 0.56% v/w oil kernel ratio.

b. Oxidative Stability Index (OSI) expressed in hours Induction Period (IP)

**Table 2** Water content of oil-ethanol emulsion, fresh ethanol and recovered ethanol separated by centrifugation after first use

	Water content % w/w		
	Ethanol 99.9%	Ethanol 95%	Ethanol 90%
Oil-ethanol emulsion	0.88	2.65	3.92
Fresh ethanol	0.09	6.5	12.2
Recovered ethanol	1.7	6.9	9.8

More water in ethanol increases the non-lipids and phospholipids content in the extracted jatropha oil. The non-lipids and phosphorus content are 0.32% / 95 ppm, 0.61% /140 ppm and 1.33% / 100 ppm for 99.9, 95 and 90% ethanol, respectively. This is in accordance with the result shown for solvent extracted soybean oil [8]. The phosphorus content reported by

these authors is 4, 10 and 2 ppm for soybean oil extracted with ethanol 99.9, 95.6 and 90%, respectively.

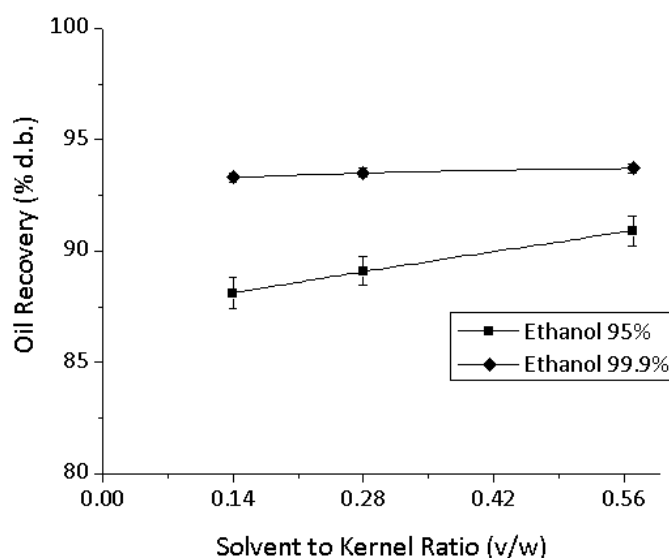
Anhydrous ethanol extracted more lipids and less non-lipids from soybean flakes compared to 95% ethanol [8]. According to Johnson and Lusas (1983) [22], the capacity to extract non-lipids increases in line with an increasing water content in ethanol. The value of the non-lipids fraction is the highest for ethanol 90% because of the high water solubility of both peptides and sugars.

The work-up of the ethanol-oil mixtures plays an important role. When ethanol is removed by centrifugation, the distribution of the phospholipids and free fatty acid between ethanol and oil determines the composition of the oil. As a result, these oils show lower phosphorus content and lower acid values than oils recovered by ethanol evaporation. The data also show that the oils obtained with the aqueous ethanol have lower phosphorus contents.

When using ethanol as the extraction solvent, its reuse is favorable from an economic point of view. However, in this case, equilibrium will be established between water in ethanol and water in the cake. Ethanol moistening can become a critical factor for the efficiency of jatropha oil extraction. Water will be absorbed from the cake into the ethanol (and vice versa) thus finally the original high purity ethanol may attract higher moisture content and lose its effectiveness after several operations. As can be seen in Table 2, the water content of recovered ethanol increased from 0.09 to 1.7% for pure ethanol (99.9% v/v). Water transfer from solid cake to ethanol will determine the desired and adequate moisture content of the kernels prior to extraction. According to Johnson and Lusas (1983) [22], kernel samples should be dried to less than 3% w.b. moisture content when using ethanol 99.9% v/v as extracting solvent in order to prevent water redistribution from solid cake to ethanol. In principle, ethanol moistening can be prevented by pressing drier kernel material.

### **5.3.3 Effect of ratio ethanol to jatropha kernels**

Experiments were conducted to optimize oil recovery as a function of the ethanol: kernel ratio; these both for ethanol 99.9 and 95% v/v (see Figure 3). When using ethanol 99.9% v/v as extracting solvent, the oil recovery is nearly independent of the solvent/kernel ratio. The oil recoveries are 93.3 and 93.6% for ethanol-kernel ratios of 0.14 and 0.56, respectively. An ethanol-kernel ratio of 0.14 is sufficient to achieve a high recovery from jatropha kernel when using ethanol 99% v/v.



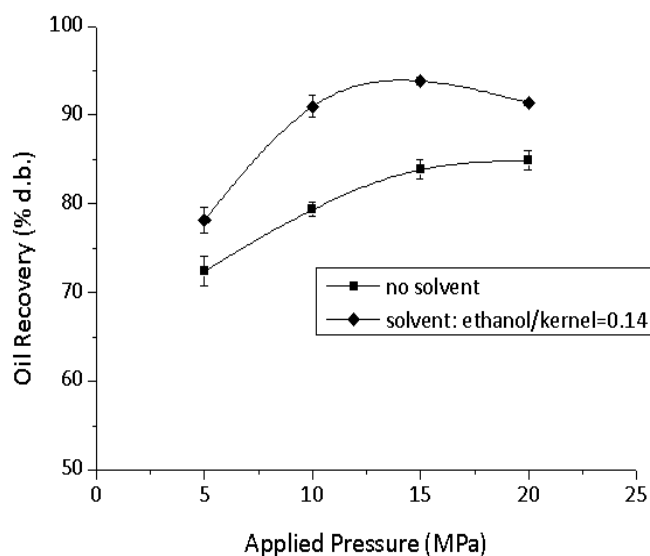
**Figure 3** Oil recoveries from jatropha kernel pressed with different ethanol kernel ratios (moisture content of kernel 3.8% w.b., applied pressure of 15 MPa, pressing temperature of 78 °C and 10 min of pressing)

For ethanol 95% v/v, the oil recovery improves upon an increase of the ethanol-kernel ratio from 0.14 to 0.56. The oil recoveries are 88.1 and 90.9% d.b. for ethanol-kernel ratios of 0.14 and 0.56, respectively. Any further increase in the solvent ratio is not likely to increase the amount of oil extracted and is envisaged to become too costly due to high recovery costs. An ethanol-kernel ratio of 0.56 is sufficient to achieve a high recovery from jatropha kernel when using ethanol 95% v/v.

#### 5.3.4 Effect of pressure

Pressure experiments were conducted using ethanol 99.9% in a pressure range of 5-20 MPa at 78 °C. Addition of ethanol at 5 and 20 MPa gave the lowest oil recovery improvement, 5.80 and 6.07, respectively. Addition of ethanol at 10 and 15 MPa gave the highest oil recovery increment, 10.28 and 9.44, respectively (see Figure 4). Pressure has two counteractive effects: increasing pressure increases the amount of ruptured cells while at the same time the compressed cake permeability is reduced which limits the drainage capability [23]. At low pressure, fewer cells are ruptured, thus reducing the amount of free-oil to be flushed by ethanol. In addition, bigger voids remaining after pressing at low pressure provide direct channeling for ethanol flow. However, increasing the applied pressure from 15 to 20 MPa reduced the oil increment percentage. This is due to the additional compaction of the cake which resulted in a more difficult flow of the ethanol oil mixture. To obtain the best permeability for the ethanol-oil mixture, there appears to be an

optimum pressure in the range of 10 or 15 MPa that should be used in the step before the flushing with ethanol.

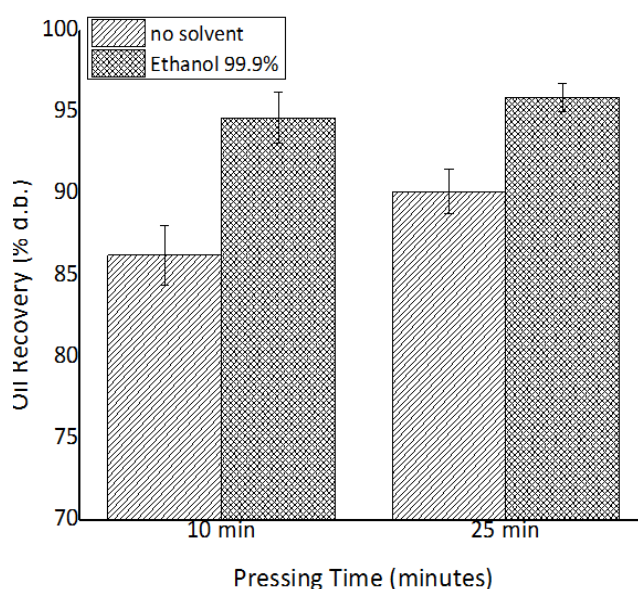


**Figure 4** Effect of applied pressure on oil recovery from jatropha kernel pressed (ratio of solvent to kernel was 0.14, v/w, ethanol 99.9%, moisture content of kernel 3.8 % w.b. pressing temperature of 78 °C)

### 5.3.5 Effect of ethanol addition at pressure step pressing

In actual continuous pressing operations such as in screw pressing, the pressure gradually increases with respect to time and direction of flow. Thus some experiments were conducted to simulate the conditions in continuous mechanical pressing. The description of the process can be seen on section 2.3.

As can be seen in Figure 5, total pressing time of 10 min gave a higher oil recovery improvement compared to total pressing of 25 min. Increasing the total pressing from 10 min to 25 min does not give any appreciable increase in oil recovery for pressing with ethanol addition. The oil recovery of ethanol-assisted jatropha pressing for 10 and 25 min is 94.7 and 95.9% d.b., respectively.



**Figure 5** Effect of pressing time on oil recovery from jatropha kernel (ratio of solvent kernel was 0.56% v/w, ethanol 99.9%, moisture content of kernel 3.8% w.b. pressing temperature of 78 °C and applied pressure increase stepwise from 5 to 25 MPa)

### 5.3.6 Mechanism of ethanol-assisted mechanical pressing

In conventional oilseed pressing, oil recovery is limited by the fact that the applied mechanical pressure has two contrary effects: on the one hand it squeezes the oil out of the seed into the inter-kernel voids of the seed-cake. This causes a build-up of fluid pressure, which acts as the driving force for oil drainage. On the other hand the seed-cake compaction leads to a decrease in permeability and thus reduces the drainage capability [23].

Several factors can be responsible for the increase in oil recovery of solvent-assisted mechanical extraction instead of conventional expression: a lower viscosity of the liquid being expressed and/or freeing of oil from the cell structure through cell disruption by ethanol. A lower viscosity of ethanol-oil compared to that of pure oils causes the increment of oil recovery. Jatropha oil viscosities are 62.58; 30.47; 19.97 and 14.07 mPas at 25, 45, 60 and 78°C, respectively. While, oil/ethanol mixtures have viscosities of 1.42; 0.93; 0.70 and 0.52 mPas at 25, 45, 60 and 78°C, respectively.

The oil/ethanol mixtures were calculated based on following equation and using viscosity ethanol data obtained from Assael et al., (1994) [16].

$$\ln (\mu) = x_1\mu_1 + x_2\mu_2$$

Where x is the mol fraction and  $\mu$  is viscosity.

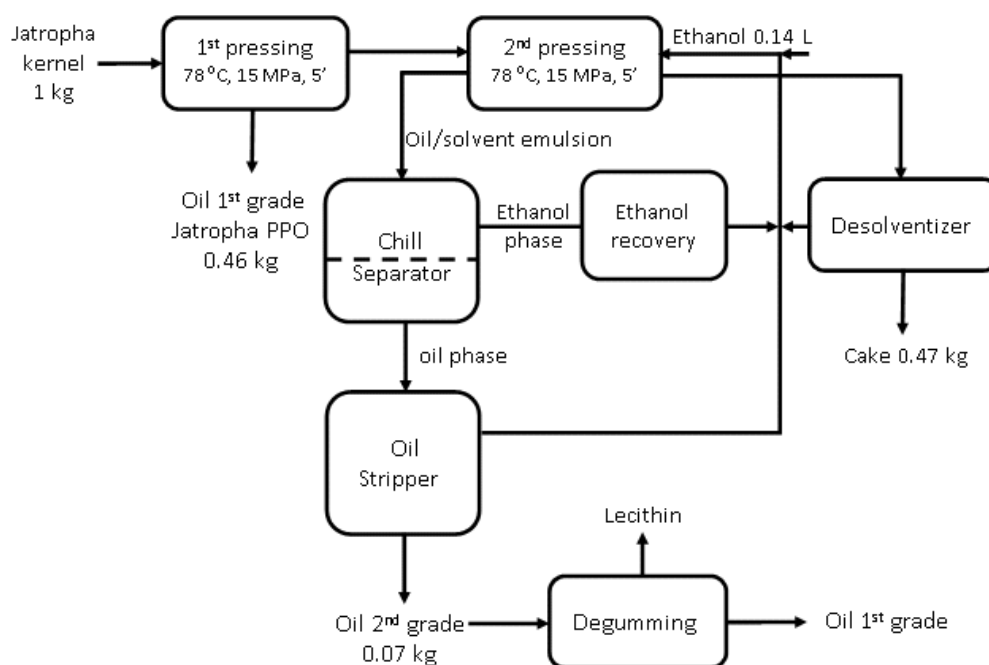
The effect of pressure in the solvent assisted pressing is the same as for conventional pressing. The compaction will reduce the void volumes in the seed-cake and thus enhance the displacement of the ethanol-oil mixture from compressed solids. On the other hand the seed-cake compaction leads to a decrease in permeability and thus reduces the drainage capability [23].

### **5.3.7 Proposed process for ethanol-assisted mechanical pressing**

Based in the results described above, a process is proposed for the ethanol-assisted mechanical pressing (See Figure 6). The first pressing is conducted using jatropha kernel with a moisture content of 3.8% w.b. at 78 °C and 15 MPa for 5 min of pressing. The oil was collected and yields good quality oil. The oil recovery at the first stage of pressing is 80% d.b. The cake from this stage of pressing is further pressed with addition of ethanol 99.9% v/v. The cumulative oil recovery after second stage of pressing is 93.3%. The ethanol-oil emulsion is further cooled and the ethanol and oil phase are allowed to separate. According to Johnson (2008) [15], the use of chill separator provides better separation. Water can be added before phase separation (centrifugation) to help increasing solvent selectivity. Water content can reduce solubility between oil and ethanol and consequently reduces ethanol content in oil-rich phase [24] and minimizes the loss of neutral oil to the ethanol-rich phase [25]. When the separated ethanol phase is recirculated, many of the soluble compounds will reach equilibrium between ethanol and oil [22]. Several processes have been devised to remove soluble compounds remaining in the ethanol phase. The remaining oil phase still contained ethanol and it removed by solvent stripping. Ethanol stripped from the oil phase can be recycled to the extraction.

Ethanol-assisted pressing provides lower solvent consumption than conventional solvent extraction. In addition, ethanol-assisted oil extraction also resulted in oils with better oxidative stability. This can be explained by the presence of phospholipids and other natural antioxidants such as tocopherol and phytates. Phospholipids have antioxidant effects due to their synergistic action with tocopherol, their metal scavenging activity and the catalytic effect to decompose hydroperoxides [26,27]. Phytates also are known as metal chelating agents [28]. However since there is a maximum limitation value for the phosphorus content in the oil, a further degumming process is needed. A study by Zufarov et al, (2008) [29] showed that reduce in phosphorus content from 96 to 7 ppm after acid degumming. In addition, the recovered phospholipids known as lecithin are valuable product as emulsifiers [22].





**Figure 6** Proposed processes for ethanol-assisted mechanical pressing of jatropha kernel

The selection of an appropriate solvent, particularly ethanol, and the addition of small quantities of water to this solvent guarantee a low loss of neutral oil during phase separation without compromising the solvent capacity of extracting free fatty acids. Nevertheless, the use of such a process in an industrial scale requires further investigations. Aspects related to the combination of the ethanol-assisted pressing and other steps of the whole refining process (degumming and deacidification) should be considered. The quality of the final product must be investigated in depth and the recovery of the solvent from the raffinate and extract streams should also be evaluated. At last, an economic analysis is necessary in order to estimate the eventual cost benefits of replacing the conventional pressing methods by the alternative solvent-assisted pressing method.

## 5.4 Conclusions

For solvent assisted pressing of jatropha kernels, ethanol is considered to be a better solvent than butanol. Porosity of the cake is an important factor before solvent assisted pressing can be conducted. Ethanol-assisted pressing results in oils with a higher phosphorus content than for oils obtained by conventional solvent-free extraction. This also leads to oils with better oxidative stability. Further phospholipids separation is an easy process. Ethanol-assisted pressing gave better oil quality when centrifugation is used as a separation method. When using ethanol 99.9% v/v as the solvent, a ratio of ethanol to kernel of 0.14 is sufficient to increase the oil recovery from jatropha kernel to 93.3% d.b.

## References

- [1] Subroto,E., Manurung,R., Heeres,H.J., and Broekhuis,A.A., 2014. Mechanical extraction of oil from *Jatropha curcas* L. kernel effect of processing parameters. *Industrial Crops and Products*, 63, 303-310.
- [2] Subroto,E., Manurung,R., Heeres,H.J., and Broekhuis,A.A., 2014. Optimization of mechanical oil extraction from *Jatropha curcas* L. kernel using response surface method. *Industrial Crops and Products*, 63, 294-302.
- [3] Rice,W.K., 1992. Mass separation of liquid or soluble components from solid materials utilizing supercritical fluids. Patent 5,169,968.
- [4] Venter,M.J., Willems,P., Kuipers, N.J.M., and de Haan, A.B., 2006. Gas assisted mechanical expression of cocoa butter from cocoa nibs and edible oils from oilseeds. *The Journal of Supercritical Fluids* 37, 350-358.
- [5] Willems,P., Kuipers,N.J.M., and de Haan,A.B., 2008. Gas assisted mechanical expression of oilseeds: Influence of process parameters on oil yield. *The Journal of Supercritical Fluids* 45, 298-305.
- [6] Dufaure,C., Mouloungui,Z., and Rigal,L., 1999. A twin-screw extruder for oil extraction: II. Alcohol extraction of oleic sunflower seeds. *Journal of the American Oil Chemists' Society* 76, 1081-1086.
- [7] Evon, P., Vandenbossche, V., Pontalier, P.Y., and Rigal, L., 2007. Direct extraction of oil from sunflower seeds by twin-screw extruder according to an aqueous extraction process: feasibility study and influence of operating conditions. *Industrial Crops and Products* 26, 351-359.
- [8] Gandhi,A.P., Joshi,K.C., Jha,K., Parihar,V.S., Srivastav,D.C., Raghunadh, P., Kawalkar, J., Jain, S.K., and Tripathi, R.N., 2003. Studies on alternative solvents for the extraction of oil-I soybean. *International Journal of Food Science and Technology* 38, 369-375.
- [9] Kwiatkowski,J.R., and Cheryan,M., 2002. Extraction of oil from ground corn using ethanol. *Journal of the American Oil Chemists' Society* 79, 825-830.
- [10] Sineiro,J., Domínguez,H., Núñez,M.J., and Lema,J.M., 1998. Ethanolic extraction of sunflower oil in a pulsing extractor. *Journal of the American Oil Chemists' Society* 75, 753-754.
- [11] Abraham,G., Hron,R.J., Kuk,M.S., and Wan,P.J., 1993. Water accumulation in the alcohol extraction of cottonseed. *Journal of the American Oil Chemists' Society* 70, 207-208.
- [12] Ferreira-Dias,S., Valente,D.G., and Abreu,J.M.F., 2003. Comparison between ethanol and hexane for oil extraction from *Quercus suber* L. fruits. *Grasas y Aceites* 54, 378-383.
- [13] Seth,S., Agrawal,Y.C., Ghosh,P.K., Jayas,D.S., and Singh,B.P.N., 2007. Oil extraction rates of soya bean using isopropyl alcohol as solvent. *Biosystems Engineering* 97, 209-217
- [14] Ye-Ni, and Zhihao-Sun, 2009. Recent progress on industrial fermentative production of acetone-butanol-ethanol by *Clostridium acetobutylicum* in China. *Applied Microbiology and Biotechnology* 83, 415-423.
- [15] Johnson,L.A., 2008. Recovery, refining, converting and stabilizing edible fats and oils. In *Food Lipids Chemistry, Nutrition, and Biotechnology*. Casimir C. Akoh and David B. Min, eds. Taylor and Francis Group, Boca Raton. 214.
- [16] Assael,M.J., and Polimatidou,S.K., 1994. Measurements of the viscosity of alcohols in the temperature range 290-340 K at pressures up to 30 MPa. *International Journal of Thermophysics* 15, 95-107.

- [17] Chien,J.T., Hoff,J.E., Lee,M.J., Lin,H.M., Chen,Y.J., and Chen,L.F., 1990. Oil extraction of dried ground corn with ethanol. *The Chemical Engineering Journal* 43, B103-B113.
- [18] Franco,D., Sineiro,J., Pinelo,M., and Núñez,M.J., 2007. Ethanolic extraction of *Rosa rubiginosa* soluble substances: Oil solubility equilibria and kinetic studies. *Journal of Food Engineering* 79, 150-157.
- [19] da Silva,C.A.S., Sanaiotti,G., Lanza,M., Follegatti-Romero,L.A., Meirelles,A.J.A., and Batista, E.A.C., 2010. Mutual solubility for systems composed of vegetable oil + ethanol + water at different temperatures, *Journal Chemical Engineering Data* 55, 440–447.
- [20] Shahidi,F., and Wanasundara,P.K.J.P.D., 2008. Extraction and analysis of lipids. In *Food Lipids Chemistry, Nutrition, and Biotechnology*. Casimir C.Akoh and David B. Min, eds. Taylor and Francis Group, Boca Raton. 126-133
- [21] Choe,E. and Min,D.B., 2006. Mechanisms and factors for edible oil oxidation. *Comprehensive Reviews in Food Science and Food Safety* 5, 169-186.
- [22] Johnson, L.A., and Lusas, E.W., 1983. Comparison of alternative solvent for oils extraction. *Journal of the American Oil Chemists' Society* 60, 229-242
- [23] Voges, S., Eggers, R., and Pietsch, A., 2008. Gas assisted oilseed pressing. *Separation and Purification Technology* 63, 1–14
- [24] Cuevas, M. S., Rodrigues, C. E.C., and Meirelles, A.J.A., 2009. Effect of solvent hydration and temperature in the deacidification process of sunflower oil using ethanol. *Journal of Food Engineering* 95, 291–297.
- [25] Rodrigues,C.E.C., Gonçalves,C.B., Batista,E., and Meirelles,A.J.A., 2007. Deacidification of vegetable oils by solvent extraction. *Recent Patents on Engineering* 1, 95-102.
- [26] Brevedan,M.I.V., Carelli,A.A., and Crapiste,G.H., 2000. Changes in composition and quality of sunflower oils during extraction and degumming, *Grasas y Aceites* 51, 417-423.
- [27] Carelli,A.A., Brevedan,M.I.V., and Crapiste,G.H., 1997. Quantitative determination of phospholipids in sunflower oils. *Journal of the American Oil Chemists' Society* 74, 511-514.
- [28] Graf, E.,Empson,K.L., and Eaton,J.W., 1987. Phytic acid: A natural antioxidant. *Journal of Biological Chemistry*, 262, 11647-11650.
- [29] Zufarov,O., Schmidt,Š., and Sekretár,S., Degumming of rapeseed and sunflower oils, *Acta Chimica Slovaca*, Vol .1, No. 1, 2008, 321 – 328.